Inorganic Chemistry

Article

pubs.acs.org/IC

Reactions of Alkyne- and Butadiyne-Derived Fluorinated Cyclophosphazenes with Diiron and Dimolybdenum Carbonyls

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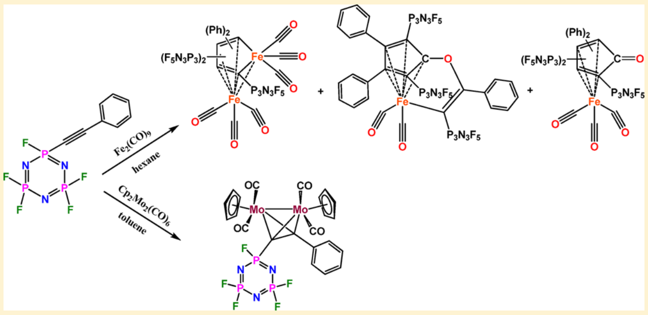
Supporting Information

ABSTRACT: The reaction of (*β*-phenylethynyl)-pentafluorocyclotriphosphazene, $[(PhC{\equiv}C)(F)PN](PNF_2)_2$, with $Fe_2(CO)_9$ in refluxing hexane resulted in five new compounds, namely, $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-}2,4\text{-}(P_3N_3F_5)_2Ph_2C_4Fe(CO)_3\}\text{-}\mu\text{-}CO]$ (**1**), $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-}2,5\text{-}(P_3N_3F_5)_2Ph_2C_4Fe(CO)_3\}\text{-}\mu\text{-}CO]$ (**2**), $[Fe(CO)_2\{\eta^5\text{-}2,5\text{-}(P_3N_3F_5)_2Ph_2C_4CO\}C(Ph){=}C(P_3N_3F_5)]$(**3**), $[Fe(CO)_3\{\eta^2{:}\eta^2\text{-}2,4\text{-}(P_3N_3F_5)_2\text{-}Ph_2C_4CO]$ (**4**), and $[Fe(CO)_3\{\eta^2{:}\eta^2\text{-}2,5\text{-}(P_3N_3F_5)_2Ph_2C_4CO]$ (**5**). While compounds **1**, **2**, **4**, and **5** have five-membered ferracyclopentadiene or cyclopentadienone rings coordinated to the $Fe(CO)_3$ unit in the $\eta^2{:}\eta^2$ mode, compound **3** has a 2,5-cyclopentadienone ring attached to an $Fe(CO)_2(P_3N_3F_5)C{=}C(Ph)$ unit, where Fe is η^5-bonded to the cyclopentadienone ring, and the carbon that is α to the phenyl unit of the $Fe(CO)_2(P_3N_3F_5)C{=}C(Ph)$ group is σ-bonded to the oxygen atom of the cyclopentadienone ring. Formation of five-membered cyclic compounds having two fluorophosphazene units on the vicinal carbon atoms of $C_4R_2R'_2Y$ rings was not observed in this reaction. No examples of $Fe(CO)_3$-bound cyclobutadiene complexes were also isolated from this reaction. A similar reaction in the presence of trimethylamine N-oxide, NMe_3O, was found to proceed at −20 °C with the formation of compounds **4** and **5** only. In contrast to the $Fe_2(CO)_9$ reaction, a reaction of alkyne-derived pentafluorocyclotriphosphazenes, $[(RC{\equiv}C)(F)PN](PNF_2)_2$ [R = Ph, $Fe(C_5H_5)_2$] with the molybdenum complex $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ (Cp = cyclopentadienyl) in refluxing toluene resulted in the simple tetrahedral clusters $Cp(CO)_2Mo(P_3N_3F_5)C{-}C(Ph)Mo(CO)_2Cp$ (**6**) and $Cp(CO)_2Mo(P_3N_3F_5)C{-}C(Fc)Mo(CO)_2Cp$ (**7**) (Fc = ferrocenyl). A similar reaction of $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ with butadiyne-derived fluorophosphazenes, $[(RC{\equiv}C{-}C{\equiv}C)(F)PN](PNF_2)_2$ [R = Ph, $Fe(C_5H_5)_2$], yielded the tetrahedral clusters $Cp(CO)_2Mo(P_3N_3F_5)C{-}C(C{\equiv}CPh)Mo(CO)_2Cp$ (**8**) and $Cp(CO)_2Mo(P_3N_3F_5)C{-}C(C{\equiv}CFc)Mo(CO)_2Cp$ (**9**) with the tetrahedral Mo_2C_2 unit forming exclusively with the alkyne unit of the butadiyne group bound to the cyclophosphazene ring. The crystal structures and infrared spectral data of these molybdenum clusters showed the presence of a semibridging carbonyl on one of the molybdenum units. All new compounds were characterized by IR, NMR [^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$] and high-resolution mass spectrometry studies. Compounds **2**, **3**, **5**, and **7**−**9** were also structurally characterized using single-crystal X-ray diffraction studies.



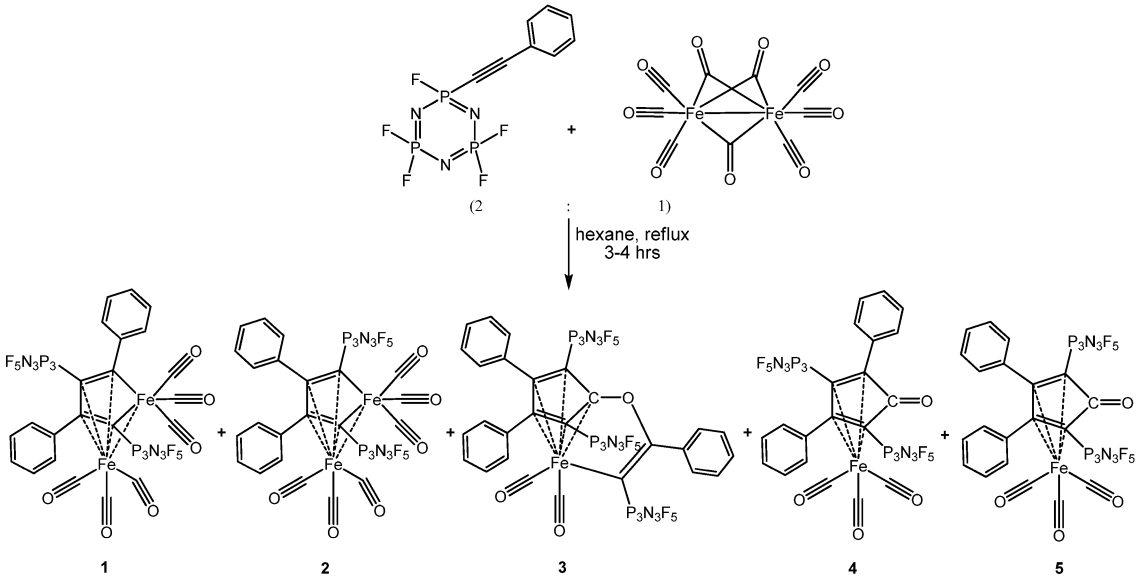
INTRODUCTION

When compared to other inorganic heterocycles, the unique spatial orientation and reactivity of the phosphorus−halogen bonds of cyclophosphazenes makes them suitable molecules for derivatization studies with a range of mono- and multifunctional substituents. In addition, the stability of the phosphazene platform allows for a wide array of organic and organometallic reactions, which can be carried out on organophosphazenes. These processes add significantly to the variety and structural complexity of available phosphazene derivatives. These attributes of the cyclophosphazene have been creatively utilized in the synthesis of hybrid inorganic−organic pendant polymers,[1] novel multidentate ligands and anions,[2−4] multiporphyrin and boron−dipyrromethane assemblies,[5] dendrimers,[6] ionic liquids, high energy density materials,[7] air-stable inclusion adducts[8] as well as compounds showing novel structural and steroisomerism unique to the cyclophosphazene skeleton.[9]

The alkyne functionality has a long-established and rich chemistry derived from reactions of metal carbonyls, which lead to numerous unique structural entities.[10] Fluorinated cyclophosphazenes are the favored trimeric phosphazenes for entry into systems with carbon−phosphorus bonds.[11g] Alkyne-derived fluorinated cyclophosphazenes are excellent precursors for realizing a range of phosphazene derivatives with diverse organic substitutents. The synthesis of alkyne-derived cyclophosphazenes, first reported in 1971,[12] was followed by exploration of its chemistry in detail by Allen and others, and they have shown the usefulness of arylethynyl-derived fluoro-

Received: July 28, 2014
Published: September 11, 2014

Scheme 1. Products Isolated from the Reaction of $P_3N_3F_5(C{\equiv}CPh)$ with $Fe_2(CO)_9$



and chlorophosphazenes in realizing novel cyclophosphazene-derived triazoles, organocobalt clusters, cobalt sandwich compounds, and cobaltacyclopentadienes; they have also shown their use in realizing multiphosphazenyl assemblies by cycloaddition reactions.[11,13]

The first examples of metal carbonyl derivatives of cyclophosphazenes were those having metal−phosphorus bonds, reported from the reactions of transition metal carbonyl anions of the type $[M(CO)_x(\eta\text{-}C_5H_5)]^-$ (M = Fe, Ru, Cr, W) with $(NPF_2)_3$ by metal−metal exchange reactions and by reactions of cyclophosphazenyl anions with organometallic electrophiles.[14−16] The chemistry reported so far on reactions of alkyne-derived cyclophosphazenes with metal carbonyls has mostly been centered on $CpCo(CO)_2$ (Cp = cyclopentadienyl) and $Co_2(CO)_8$.[11] While the former resulted mostly in cyclodimerization reactions of the alkynes, the latter gave the tetrahedral cluster wherein the Co−Co bond was retained as well as the metal free cyclotrimerized product.[10c,11,13a] In contrast to the routine chemistry of $Co_2(CO)_8$, other di- and trinuclear metal carbonyls have been found to react in general with alkynes resulting in novel and complex structures often involving metal−metal bond cleavage. For example, reactions of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ with alkynes have been found to result in a plethora of structural types and many products having practical use in organic chemistry,[17] the most important among them being the synthesis of substituted cyclopentadienones and cyclobutenediones and conversion of alkynes to cyclic imides and anhydrides.[18] Also, there are reports on $Fe_2(CO)_9$ and $Cp_2Mo_2(CO)_4(RCCR)$ being used as catalysts for reduction of alkynes to alkenes.[19] Herein we report the first reactions of dinuclear metal carbonyls, specifically, $Fe_2(CO)_9$ and $Cp_2Mo_2(CO)_6$, with alkyne- and butadiyne-derived fluorinated cyclotriphosphazenes derivatives. This new chemistry provides phosphazene substituents of interest that are inaccessible by other methodologies. Additionally, the structure and properties of the new, novel phosphazene derivatives obtained from such a study are compared.

■ RESULTS AND DISCUSSION

An initial examination of the reaction of (*β*-phenylethynyl)-pentafluorocyclotriphosphazene, $P_3N_3F_5C{\equiv}CPh$, with $Fe(CO)_5$ showed that the process was slow and yielded very low yields of unidentified products. To improve the reactivity, the use of $Fe_2(CO)_9$ was explored. This dinuclear species provides the kinetically active, coordinatively unsaturated species $Fe(CO)_4$.[17] This expectation proved to be correct since the reaction of $P_3N_3F_5C{\equiv}CPh$ with $Fe_2(CO)_9$ in a 2:1 molar ratio was found to proceed in refluxing hexane with the formation of compounds **1** to **5** (Scheme 1). The compounds **1** and **2** were isomers of fluorophosphazene-derived ferracyclopentadiene metallacycles bound to the $Fe(CO)_3$ unit in an $\eta^2{:}\eta^2$-mode, and compounds **4** and **5** were isomers of fluorophosphazene carbonyl insertion-derived cyclopentadienone rings bound to $Fe(CO)_3$ units in a similar fashion. Compounds **2**, **3**, and **5** were structurally characterized, whereas compounds **1** and **4** were assigned structures on the basis of ^{31}P NMR, IR spectroscopy, and high-resolution mass spectrometry (HRMS) studies. The atypical molecular structure of compound **3** consists of a (2,5-diphosphazenyl)-cyclopentadienone ring attached to an $Fe(CO)_2(P_3N_3F_5)C{=}C(Ph)$ unit, where Fe is η^5-bonded to the cyclopentadienone ring, the alkene carbon that is α to the phenyl unit σ-bonded to the oxygen atom of the cyclopentadienone ring, and the alkene carbon that is α to the $P_3N_3F_5$ unit σ-bonded to the Fe atom. It is interesting to note that the formation of five-membered cyclic compounds having two fluorophosphazene units on the vicinal carbon atoms of $C_4R_2R'_2Y$ rings as well as examples of $Fe(CO)_3$-bound cyclobutadiene complexes or cyclotrimerized products were not observed in this reaction.

The compounds **1** and **2** are possibly formed by the oxidative coupling of two $P_3N_3F_5C{\equiv}CPh$ molecules with an $Fe(CO)_3$ unit to give ferracyclopentadiene ring, which is η^4-bound to another $Fe(CO)_3$ unit, which in turn is attached to the ring Fe through a direct Fe−Fe bond. Molecular structure of compound **2** showed that one of the CO groups of the diene-bound $Fe(CO)_3$ moiety was significantly bent, with Fe−C−O = 167.73(4)°, indicating it to be in a semibridging mode. This was further supported by IR spectroscopy, which showed a

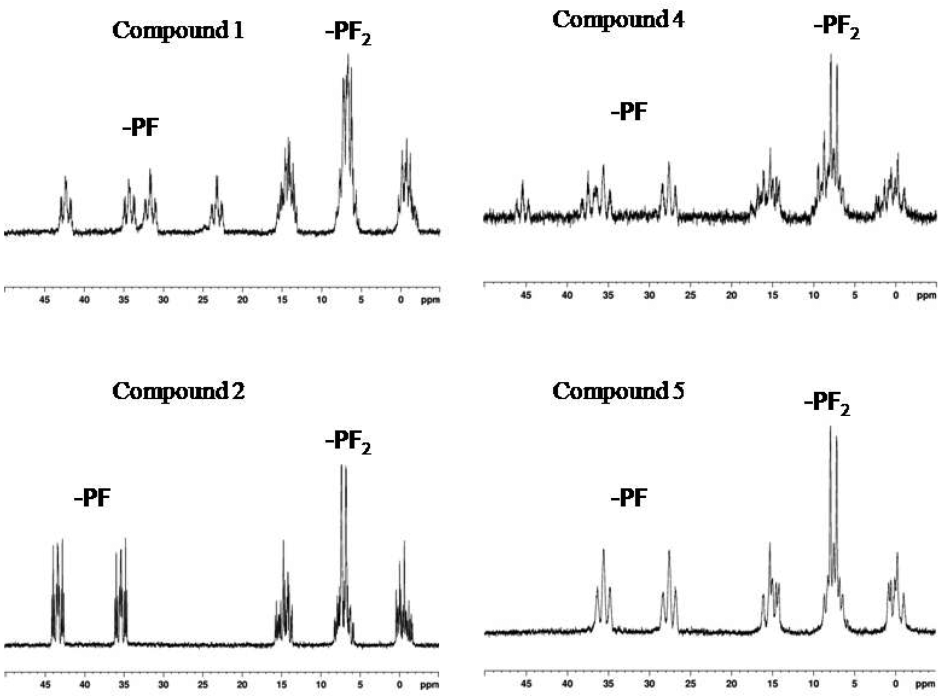


Figure 1. $^{31}P\{^1H\}$ NMR of compounds **1**, **2**, **4**, and **5**.

strong ν_{CO} band at 1998 cm^{-1} distinct from other ν_{CO} bands of **2** (2012–2088 cm^{-1}). Moreover, compound **5** whose crystal structure showed no semibridging carbonyls did not show any band less than 2040 cm^{-1}. Compound **1** showed the presence of two different types of phosphazene units in its ^{31}P NMR spectra as it gave two different sets of doublet multiplet peaks for the P–F region (Figure 1).

Compound **1** was assigned a structure similar to **2** as both these compounds gave peaks in their mass spectra at 663.45, corresponding to the butadiene fragment (Figure 2). These butadiene fragments are possibly formed by the removal of two Fe(CO)$_3$ fragments from compounds **1** and **2**. The identity of compound **1** was further confirmed by IR spectroscopy as both compounds **1** and **2** gave similar type of peak pattern for the CO region. So, based on ^{31}P NMR, IR, and mass spectral studies, the structure of compound **1** was assigned as the 2,4-diphosphazenyl isomer of the Fe(CO)$_3$-bound ferracyclopentadiene. The possibilities of **1** being a 3,4-diphosphazenyl isomer of ferracyclopentadiene ring or a compound having cyclobutadiene ring bound to Fe(CO)$_3$ were eliminated as both of these would have the phosphazene units in the same environment. In addition, a 3,4-diphosphazenyl-substituted isomer will result in two cyclophosphazene units on the vicinal carbon atoms of the five-membered $C_4R_2R'_2Y$ rings, which has been ruled out from previous studies on cobaltacyclopentadiene-based metallacylcles.[12d,e]

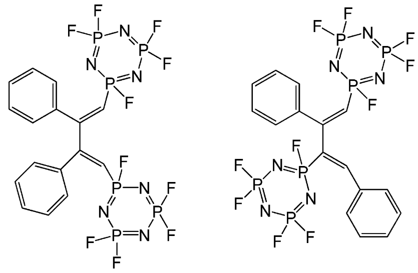
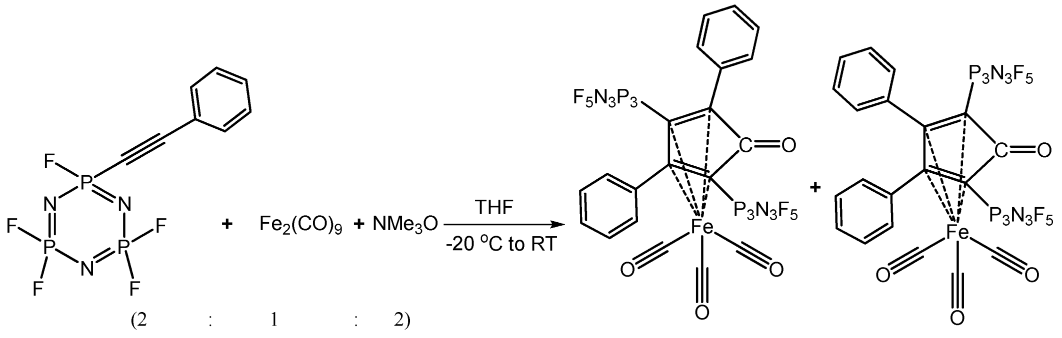


Figure 2. Diphosphazenyl butadiene units of compounds **1** and **2**.

The compounds **4** and **5** are formed by [2 + 2 + 1] cycloaddition[18c] of two $P_3N_3F_5C{\equiv}CPh$ molecules with one CO molecule to give a cyclopentadienone ring, which is η^4-bound to an Fe(CO)$_3$ unit. Compound **4** also gave two peaks for the P–F region in its ^{31}P NMR spectra, indicating it as having a 2,4-isomer of the cyclopentadienone ring (Figure 1). The isomeric compounds **4** and **5** gave the same HRMS peak at *m*/*z* 852.82 for the expected compound. The identity of compound **4** was further supported by IR spectroscopy as it gave a peak around 1670 cm^{-1} (apart from peaks corresponding to the Fe(CO)$_3$ moiety) corresponding to the cyclopentenone C=O group, which was also observed in the spectra of compound **5** at 1669 cm^{-1}. These cyclopentadienone $\nu_{C=O}$ values are in agreement with the analogous nonphosphazenyl compound $[Fe(CO)_3\{\eta^2:\eta^2\text{-}2,5\text{-}Fc_2C_4H_2CO\}]$ (Fc = ferrocenyl) ($\nu_{C=O}$ = 1657 cm^{-1}).[20] Compounds **1**–**3** are yellow in color, whereas compounds **4** and **5** are red in color. Apart from compounds **1** to **5**, thin-layer chromatography (TLC) analysis showed the presence of a faint red spot between the second and third yellow spots, which was found to be highly unstable and decomposed on the column making its isolation impossible. Out of the isolated five compounds, red compounds were found to be the most unstable as they decompose rapidly in solution. The unsymmetrical isomers (compounds **1** and **4**) were found to be relatively more unstable compared to their symmetrical analogues (compounds **2** and **5**). Compound **5**, although unstable in solution form, was found to be highly stable in the solid state. Compound **4** was found to be the most unstable among the five compounds separated.

A reaction carried out in the presence of excess of alkyne (4:1) was found to give similar products with no noticeable changes in the yields except the fact that compound **4** was not

Scheme 2. Reaction of $P_3N_3F_5(C{\equiv}CPh)$ with $Fe_2(CO)_9$ in the Presence of Trimethylamine N-oxide



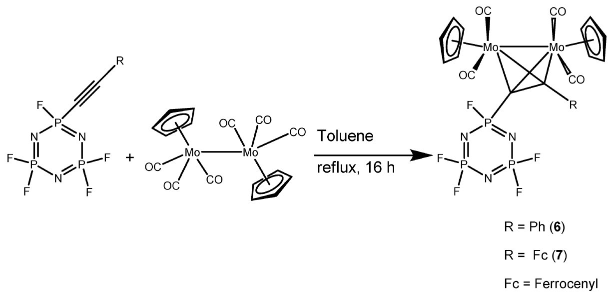
4

5

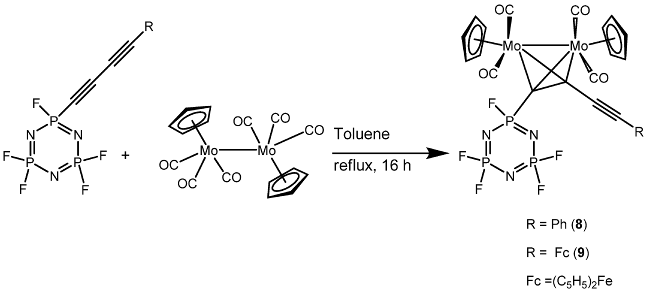
formed. Interestingly, a reaction of $P_3N_3F_5C{\equiv}CPh$ with $Fe_2(CO)_9$, when attempted in the presence of an activator, trimethylamine N-oxide, in 2:1:2 molar ratio, was found to proceed at −20 °C with the formation of cyclopentadienone ring-bound compounds **4** and **5** only, in 3% and 18% yield, respectively (Scheme 2). Further heating of the reaction mixture led to the total decomposition of all the products. Our attempts to increase the yields of compounds **4** and **5** by carrying out the same reaction in 4:1:2 and 4:1:1 molar ratios were also unsuccessful as there were no noticeable changes observed in the yield of compounds, and unreacted alkyne was recovered from such reactions.

The success of the reactions of the binuclear iron species led us to explore other binuclear metal carbonyls. A reaction of $N_3P_3F_5(C{\equiv}CR)$ [R = Ph, $Fe(C_5H_5)_2$] with $Cp(CO)_3Mo-Mo(CO)_3Cp$ in refluxing toluene yielded the first examples of phosphazene-derived molybdenum carbonyl clusters $Cp(CO)_2Mo(P_3N_3F_5)C-C(Ph)Mo(CO)_2Cp$ (**6**) and $Cp(CO)_2Mo(P_3N_3F_5)C-C(Fc)Mo(CO)_2Cp$ (**7**) (Scheme 3). The reaction possibly goes through the $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ intermediate, which is known to form under refluxing toluene.[21] Compound **7** was structurally characterized, whereas compound **6** was characterized by NMR, IR, and HRMS studies. The molecular structure of compound **7** showed that two of the CO groups are in the semibridging mode, which was further supported by IR spectroscopy (ν = 1872 cm^{-1}). The IR spectra of compound **6** also indicated the presence of semibridging carbonyls (ν = 1862 cm^{-1}). Unlike the reported reactions of $Co_2(CO)_8$ with the geminally disubstituted compound *gem*-$N_3P_3F_4(C{\equiv}CR)_2$,[11c] reactions of $Cp_2Mo_2(CO)_6$ with such derivatives of fluorophosphazene in 1:1 or 1:2 molar ratio resulted in decomposed products. The reactions with butadiyne-derived fluorophosphazenes $P_3N_3F_5(C{\equiv}C-C{\equiv}CR)$ [R = Ph, $Fe(C_5H_5)_2$] yielded the tetrahedral clusters $Cp(CO)_2Mo(P_3N_3F_5)C-C(C{\equiv}CPh)Mo(CO)_2Cp$ (**8**) and $Cp(CO)_2Mo(P_3N_3F_5)C-C(C{\equiv}CFc)Mo(CO)_2Cp$ (**9**) with the Mo_2C_2 unit forming exclusively with one of the alkyne units of the butadiyne group bound to the cyclophosphazene ring (Scheme 4). Both compounds **8** and **9** also indicated the presence of semibridging carbonyls in their molecular structures, which was supported by IR spectroscopy. Compounds **8** and **9** are the first examples of carbonyl clusters derived from butadiyne-based cyclophosphazenes.

Scheme 3. Reaction of $P_3N_3F_5(C{\equiv}CR)$ with $Cp_2Mo_2(CO)_6$



Scheme 4. Reaction of $P_3N_3F_5(C{\equiv}C-C{\equiv}C\text{-}R)$ with $Cp_2Mo_2(CO)_6$



Spectral Studies on Compounds 1−9. The ^1H NMR chemical shifts for the phenyl region of compounds **1** and **4**, having the phosphazene rings unsymmetrically placed on the five-membered ring, differs considerably from that of the analogous symmetrically substituted compounds **2** and **5**. Compounds **2** and **5** gave two sets of multiplets in the region of 6.95−7.09 ppm (compound **2**) and of 7.37−7.49 ppm (compound **5**) with the integration ratio 6:4, whereas compounds **1** and **4** gave complex multiplets in the range of 6.83 to 7.48 ppm, which indicated the lesser symmetry of molecules **1** and **4**. Phenyl protons of the cyclopentadienone derivatives (compound **4** and **5**) were found to be slightly more deshielded compared to the corresponding ferracyclopentadiene derivatives (compounds **1** and **2**). In compound **3**, alkene-bound phenyl protons were found to be deshielded (7.55−7.38 ppm) compared to the cyclopentadiene-bound phenyl groups of the same compound (7.33−7.19 ppm).

In the case of compounds **1** and **4**, where the phosphazene units are unsymmetrically placed, the two PF moieties are present in different environments and hence have different chemical shifts in their ^{31}P and ^{19}F-NMR spectra, whereas symmetrical compounds **2** and **5** have only one signal for the PF moieties as both phosphazene units are in the same environment (Figure 1). The ^{31}P NMR chemical shifts

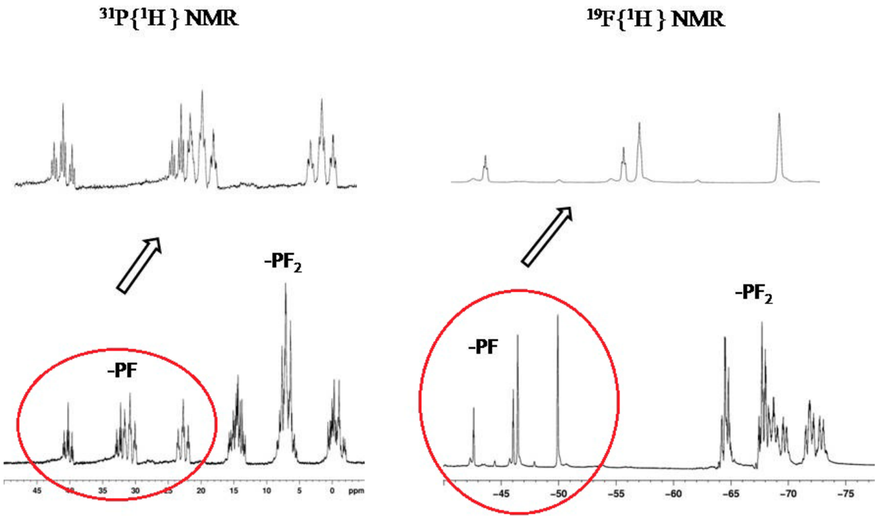


Figure 3. $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR of compound **3** with expansion of P−F signals.

corresponding to the PF moiety for compounds **2** and **5** were observed as doublet multiplets at 39.42 and 31.60 ppm, respectively, whereas for compounds **1** and **4**, these were observed as different sets of doublet multiplets at 27.36 and 38.32 ppm for compound **1** and at 31.58 and 41.43 ppm for compound **4**. In the ^{31}P NMR spectra of **1**, the signal at 27.36 ppm is due to the PF(C) group that is away from the metal center, and the signal at 38.32 ppm is due to the PF(C) group that is nearer to the metal center. Similarly, for the ^{31}P NMR of compound **4**, the signal at 31.58 ppm is due to the PF(C) group that is nearer to the C═O group of the cyclopentadienone ring, and the signal at 41.43 ppm is due to the PF(C) group that is distant from the C═O group of the cyclopentadienone ring. The signals corresponding to the PF_2 moiety in the ^{31}P NMR spectra were observed in the range of 6.67−7.92 ppm for compounds **1**−**5**. The ^{19}F-NMR spectra of compounds **1**−**5** gave doublet of multiplet peaks in the range from −62.03 to −72.88 ppm for the PF_2 groups due to the diastereotopic nature of the fluorine atoms of the $N_3P_3F_5$ units. Similar to ^{31}P NMR, ^{19}F NMR also gave two sets of doublet multiplet peaks for the PF moiety for the unsymmetrical compounds **1** and **4** and a single doublet multiplet peak for the symmetrical compounds **2** and **5**.

The ^{31}P NMR of compound **3** also showed two sets of doublet multiplets at 26.77 and 36.27 ppm for two different types of phosphazene moieties, one attached to cyclopentadienyl ring and the other bound to the alkene unit. The ^{19}F-NMR spectra of compound **3** also showed two sets of signals at −44.30 and −48.19 ppm for the PF moiety confirming two types of phosphazene groups present on this molecule. It was of interest to observe that, unlike compounds **1** and **4**, where two types of P−F moieties showed a similar type of peak-splitting pattern in ^{31}P and ^{19}F NMR, compound **3** showed a different type of splitting pattern for two types of P−F moieties (Figure 3). This is because, in compounds **1** and **4**, both the phosphazene rings are connected to the same type of ring, whereas in compound **3**, two of the phosphazene rings are attached to the cyclopentadiene ring, and one phosphazene ring is attached to the alkene. In ^{19}F-NMR also one of the P−F signal (at −44.30 ppm) was observed as doublet of triplet, whereas the other signal at −48.19 ppm was observed as a simple doublet.

The ^{13}C NMR δ values for the metal-bound CO groups were found to be in the range of 215.49−190.21 ppm for compounds **1**−**5**, whereas the signal for the cyclopentadienone CO group was observed at 171.41 ppm for compound **4** and at 171.23 ppm for compound **5**. The IR spectral studies probing the carbonyl units of compounds **1** and **2** gave similar ν_{CO} bands in the region from 2088 to 1963 cm^{-1}. Both compounds **1** and **2** showed the presence of semibridging carbonyl groups at 1963 and 1998 cm^{-1}, respectively, which was further confirmed by X-ray diffraction study carried out on compound **2**. Compounds **3**−**5** gave ν_{CO} bands in the region from 2035 to 2105 cm^{-1}. Compounds **4** and **5** also gave peaks at 1670 and 1669 cm^{-1}, respectively, corresponding to the cyclopentadienone carbonyl group.

The ^1H NMR of compounds **6**−**9** showed the signal corresponding to the molybdenum-bound cyclopentadiene ring in the region of 5.28−5.44 ppm. The signal corresponding to molybdenum-bound Cp was found to be shifted downfield as the alkyne changed to butadiyne. The ^{31}P NMR of molybdenum clusters **6**−**9** gave doublet multiplet peaks in the range of 51.36−53.35 ppm for the PF(C) moiety and triplet multiplet peaks in the range of 7.67−8.26 ppm for the PF_2 moiety. Similarly, the ^{19}F NMR of compounds **6**−**9** gave doublets in the range of −46.56 to −53.35 ppm for the PF(C) moiety and doublet multiplets in the range from −67.01 to −69.02 for the PF_2 moiety. The ^{13}C NMR of molybdenum compounds gave two signals for the CO groups in the region from 225.09 to 227.19 ppm, and the Mo-bound cyclopentadiene ring was observed at 92.29−93.11 ppm. All molybdenum clusters showed the presence of one semibridging carbonyl group in their IR spectra in the range of 1862−1872 cm^{-1}, which was further confirmed by X-ray diffraction studies for compounds **7**−**9**. The free alkyne units of **8** and **9** were found to show their $\nu_{C\equiv C}$ stretching bands at 2195 and 2181 cm^{-1}, respectively.

X-ray Crystal Structures of Compounds 2, 3, 5, and 7−9. The crystal structures of compounds **2**, **3**, **5**, and **7**−**9** are given in Figures 4−9. Crystallographic data and data collection parameters are given in Table 1, and bond lengths and bond angles are given in the Supporting Information. The phosphazene rings were found to be almost planar in compounds **2**, **3**, **7**, and **9** as the substituted phosphorus atom and the opposite-ring nitrogen atom were not found to

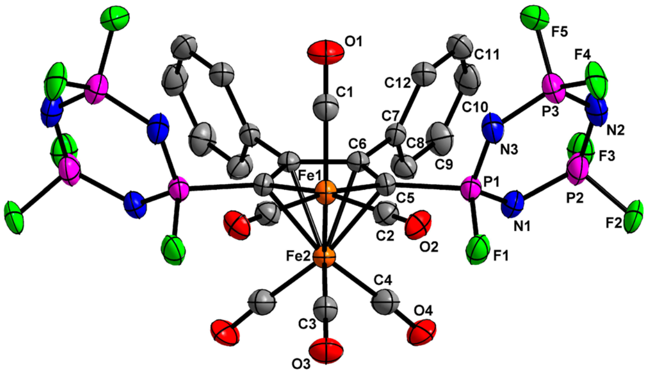


Figure 4. ORTEP diagram of compound **2** with thermal ellipsoids at the 30% probability level.

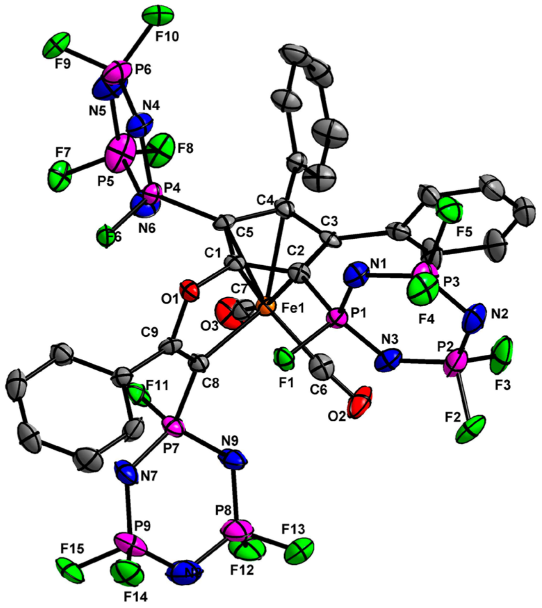


Figure 5. ORTEP diagram of compound **3** with thermal ellipsoids at the 30% probability level.

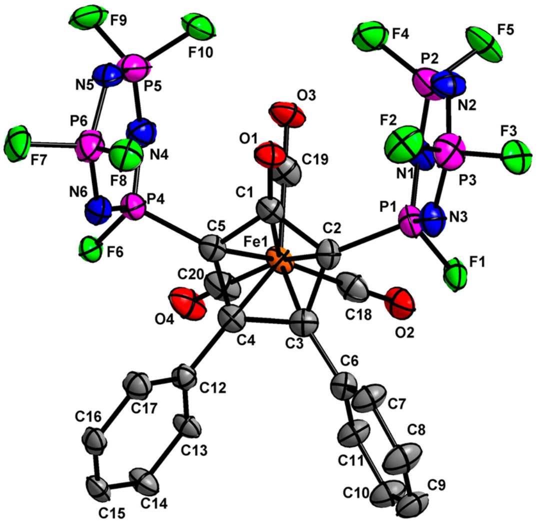


Figure 6. ORTEP diagram of compound **5** with thermal ellipsoids at the 30% probability level.

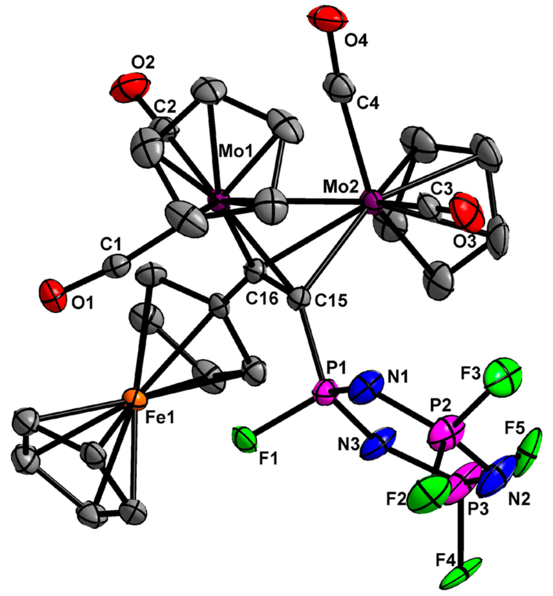


Figure 7. ORTEP diagram of compound **7** with thermal ellipsoids at the 30% probability level.

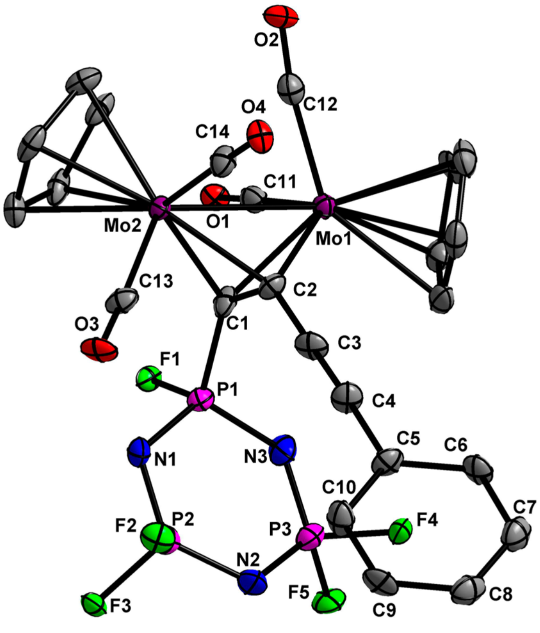


Figure 8. ORTEP diagram of compound **8** with thermal ellipsoids at the 30% probability level.

deviate significantly from the mean plane defined by the other four atoms of the heterocycle. In contrast, the conformation of the P_3N_3 rings of **5** and **8** was more toward a half chair. The two phosphazene rings substituted on the five-membered cyclopentadienone/ferracyclopentadiene ring of compounds **2**, **3**, and **5** were in the eclipsed form. The P−F bond lengths of the substituted phosphorus atom for the ferracyclopentadiene-substituted compound **2** [1.553(2) Å] were found to be larger than the cyclopentadienone-substituted compound **5** [1.529(3) and 1.534(3) Å]. The P−C bond distances for the $Fe(CO)_n$-bound compounds **2**, **3**, and **5** were found to be in the range of 1.739(6)−1.785(6) Å, which is longer than the P−C bond distance observed for the molybdenum cluster compounds, namely, **7**−**9** [1.708(6)−1.713(4) Å]. In compound **3**, the P−

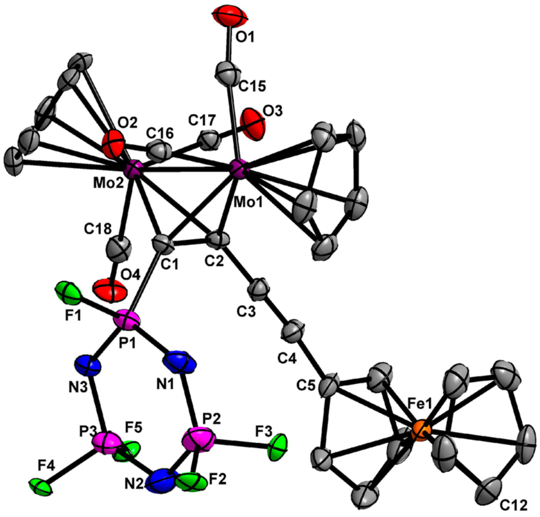


Figure 9. ORTEP diagram of compound **9** with thermal ellipsoids at the 30% probability level.

C bond length for the alkene-bound phosphazene unit was found to be 1.739(6) Å, which is shorter than the P−C bond length of the cyclopentadiene-substituted phosphazene units [1.785(6) Å] present in the same molecule (Figure 5).

The Fe of ferracyclopentadiene ring in compound **2** was found to be in a square pyramidal geometry with one of the CO groups attached to this iron atom oriented nearly perpendicular to the ferracyclopentadiene ring, similar to the earlier reported structures[20] (Figure 4). The ferracyclopentadiene ring in compound **2** and the cyclopentadienone ring in compound **5** were not planar, whereas the cyclopentadiene ring of compound **3** was found to be perfectly planar confirming its η^5 bonding mode. The Fe atom of the ferracyclopentadiene ring of compound **2** and the CO unit of the cyclopentadienone ring of compound **5** were found to be out of plane with angles of 14.8(2)° and 23.1(3)°, respectively. The two phosphazene rings of compounds **2**, **3**, and **5** were found to be oriented with dihedral angles of 63.9(4), 57.6(7), and 39.9(5)°, respectively. The Fe(1)−Fe(2) bond distance in compound **2** was found to be 2.545(1) Å, which is comparable to earlier reported ferrole complexes.[20] The C−O bond distance for the cyclopentadienone CO group was found to be 1.212(4) Å in compound **5** and 1.368(7) Å for compound **3**. The alkene bond length C(8)−C(9) was found to be 1.342(9) Å in compound **3**, which is comparable [1.339(3) Å] to compound [Fe(CO)$_2${η^5-2,5-Fc$_2$C$_4$H$_2$CO}C(Fc)=CH], the only other structurally characterized example known in the literature.[20] The Mo(1)−Mo(2) bond distance was found to be in the range of 2.964(8)−2.988(8) Å for compounds **7**−**9**. On forming the tetrahedral cluster, the C−C distance of the reacting alkyne part was found to be in the range of 1.388(7) to 1.402(6) Å for compounds **7**−**9**, while the bond lengths of the unreacted alkyne for the butadiyne compounds **8** and **9** were found to be 1.224(9) and 1.184(7) Å, respectively. The dihedral angles between the two cyclopentadiene rings attached to the molybdenum atoms were found to be 40.1(3), 33.53(3), and 34.3(2)°, respectively, for compounds **7**−**9**.

One of the carbonyl groups in compound **2** (C_3O_3) was found to be significantly bent, with an angle Fe(2)−C(3)−O(3) = 167.7(4)°, indicating it to be in semibridging mode. Compound **7** also showed two of its carbonyl groups (C_1O_1

Table 1. X-ray Crystal Structure Parameters of Compounds 2, 3, 5, 7, 8, and 9

parameters	2	3	5	7	8	9
formula	$C_{22}H_{10}F_{10}Fe_2N_6O_6P_6$	$C_{27}H_{15}F_{15}FeN_9O_3P_9$	$C_{20}H_{10}F_{10}FeN_6O_4P_6$	$C_{26}H_{19}F_5FeMo_2N_3O_4P_3$	$C_{24}H_{15}F_5Mo_2N_3O_4P_3$	$C_{28}H_{19}F_5FeMo_2N_3O_4P_3$
MW	941.88	1133.06	830.01	873.08	789.18	897.10
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/m$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	8.929(3)	14.063(3)	15.215(3)	10.031(2)	8.355(1)	8.291(2)
b /Å	22.930(8)	15.562(3)	10.924(2)	10.601(3)	11.081(1)	12.889(3)
c /Å	9.205(3)	19.314(4)	19.809(4)	15.137(4)	15.788(2)	14.814(4)
α (deg)	90.00	90.00	90.00	77.944(4)	69.946(2)	81.028(4)
β (deg)	117.449(6)	90.00	109.111(4)	76.747(4)	84.218(2)	87.829(4)
γ (deg)	90.00	90.00	90.00	71.353(4)	84.831(2)	83.208(4)
V /Å^3	1672.3(10)	4226.8(15)	3111.0(10)	1468.5(6)	1363.7(3)	1552.4(7)
Z	2	4	4	2	2	2
T /K	298(2)	298(2)	298(2)	298(2)	150(2)	298(2)
λ /Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ_c (g/cm3)	1.870	1.781	1.772	1.975	1.922	1.919
μ (mm^{-1})	1.259	0.809	0.893	1.563	1.168	1.482
goodness of fit	1.277	1.173	0.998	1.166	1.155	1.093
θ range	1.78−25.00	1.68−25.00	1.48−25.00	1.40−25.00	1.38−25.00	1.39−25.00
total reflections	16 193	40 807	28 974	7645	6862	14 894
unique reflections	3031	7451	5470	5164	4332	5461
observed data [$I > 2\sigma(I)$]	2412	6678	3236	4435	3891	4477
R_{int}	0.0833	0.0772	0.0848	0.0240	0.0215	0.0486
R_1,^{a} wR_2^{a} [($I > 2\sigma(I)$]	0.0883, 0.1540	0.0713, 0.1372	0.0520, 0.1024	0.0389, 0.1073	0.0396, 0.1274	0.0452, 0.0849
R_1,^{a} wR_2^{a} (all data)	0.1142, 0.1636	0.0810, 0.1412	0.1040, 0.1181	0.0480, 0.1274	0.0473, 0.1476	0.0605, 0.0900

$^aR_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$; $wR_2 = \Sigma[(|F_0|^2 - |F_c|^2)^2]^{1/2}$.

and C_4O_4) deviating from linearity compared to other carbonyls. As a result, Mo(1)−C(1) [1.992(4) Å] and Mo(2)−C(4) [1.977(7) Å] bond distances were found to be shorter than the other Mo−C bond lengths of carbonyl groups, and C(1)−O(1) [1.147(6) Å] and C(4)−O(4) [1.149(9) Å] bond lengths were found to be longer than the C−O bond lengths of other carbonyl groups of **7** [1.135(7)−1.137(8) Å]. In contrast to compound **7**, butadiyne derivatives **8** and **9** showed only one of their carbonyls to be in semibridging mode, which is in agreement with analogous clusters of $Cp_2Mo_2(CO)_4$ with symmetrical aryl butadiynes PhC≡C−C≡CPh[22] and (4-Py)C≡C−C≡C(4-Py) (Py = pyridine).[23]

■ EXPERIMENTAL PROCEDURE

General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under nitrogen atmosphere. All the solvents were freshly distilled using standard procedures. The compounds hexafluorocyclotriphosphazene,[24] $P_3N_3F_5$(C≡CPh),[11c] $P_3N_3F_5$(C≡CFc),[13c] $P_3N_3F_5$(C≡C−C≡C−R) (R = Ph, Fc),[13a] and dicyclopentadienyl dimolybdenum hexacarbonyl[25] were prepared according to literature procedures. $N_3P_3Cl_6$, *n*-BuLi (1.6 M in hexane), diiron nonacarbonyl, and trimethylamine N-oxide were procured from Aldrich and used as such.

Instrumentation. The ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, 282.37, and 121.48 MHz, respectively, using $CDCl_3$ as a solvent. IR spectra in the range of 4000−250 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Mass spectra were recorded on a Bruker Micro-TOF QII quadrupole time-of-flight (Q-TOF) mass spectrometer.

X-ray Crystallography. Suitable crystals of compounds **2**, **3**, **5**, **7**, **8**, and **9** were obtained by slow evaporation of their saturated solutions in ethyl acetate/hexane or dichloromethane/tolune solvent mixtures. The single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a Mo Kα (λ = 0.710 73 Å) sealed tube. All crystal structures were solved by direct methods. The program SAINT (version 6.22) was used for integration of the intensity of reflections and scaling. The program SADABS was used for absorption correction. The crystal structures were solved and refined using the SHELXTL (version 6.12) package.[26] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Reaction of $P_3N_3F_5$(C≡CPh) with $Fe_2(CO)_9$. To a solution of $Fe_2(CO)_9$ (0.22 g, 0.60 mmol) in 40 mL of dry hexane was added a solution of $P_3N_3F_5$(C≡CPh) (0.40 g, 1.2 mmol) in 20 mL of dry hexane, and the mixture was refluxed with stirring for 3−4 h. During the course of reaction the reaction mixture changed from yellowish-brown to reddish-brown. Afterward, all solvents were removed by evaporation, and the crude product was subjected to column chromatography over silica gel using ethyl acetate/hexane as eluent. The first fraction, which came out in pure hexane, was characterized as the unreacted $P_3N_3F_5$(C≡CPh) (80 mg). Further elution with 1% ethyl acetate/hexane mixture gave a yellow band containing three yellow spots. Further elution with 2% ethyl acetate/hexane mixture gave a red band containing two red spots. These two fractions were separately subjected to chromatographic workup using silica gel TLC plates. Use of a 0.5% solution of ethyl acetate/hexane for the yellow fraction and 1% solution for red fraction separated the following five compounds in the order of elution.

*Compound **1***. Yellow semisolid, yield: 41 mg, 7.21%. IR (ν, cm^{-1}): 2917vs, 2849m, 2361w, 2088s, 2062vs, 2040s, 2015vs, 1963s, 1268vs, 950s, 836s. ^{1}H NMR ($CDCl_3$, ppm): δ 7.48−6.83 (m, 10H, Ph*H*). ^{13}C {^{1}H} NMR: δ 208.30, 206.87, 201.22, 190.21 (CO), 148.26, 131.00, 130.95, 130.20, 129.77, 129.58, 128.92, 128.59, 128.39, 128.30, 128.22, 127.69, 125.81, 123.18. ^{31}P{^{1}H} δ 6.67 [tm, $^1J_{P-F}$ = 900 Hz, −*P*F$_2$], 27.36 [dm, $^1J_{P-F}$ = 1020 Hz, −*P*F(C)], 38.32 [dm, $^1J_{P-F}$ = 976 Hz, −*P*F(C)]. ^{19}F{^{1}H} NMR: δ −39.83 [d of t, $^1J_{P-F}$ = 971 Hz, $^2J_{P-F}$ = 11.43 Hz, −P*F*(C)], −43.35 [d of t, $^1J_{P-F}$ = 1019 Hz, $^2J_{P-F}$ = 10.87 Hz, −P*F*(C)], −62.03 to −67.83 [complex mixture of doublets, −P*F*$_2$], −70.25 [dm, J_{P-F} = 954 Hz, −P*F*$_2$]. Low-resolution mass spectrometry (LRMS): Calcd for $C_{16}H_{12}F_{10}N_6P_6$ $[M - Fe_2CO_6]^+$: 663.9389, Found: 663.4504.

*Compound **2***. Yellow solid, yield: 85 mg, 14.93%. mp: 146−148 °C.Found: C, 28.15; H, 1.06; N, 8.81. Anal. Calcd (%) for $C_{22}H_{10}F_{10}Fe_2N_6O_6P_6$: C, 28.05; H, 1.07; N, 8.92. IR (ν, cm^{-1}): 2961m, 2918s, 2849m, 2360w, 2088s, 2057vs, 2038s, 2012vs, 1998s, 1256vs, 1096br, 940s, 839s. ^{1}H NMR ($CDCl_3$, ppm): δ 7.09 (m, 6H, Ph*H*), 6.95 (m, 4H, Ph*H*). ^{13}C {^{1}H} NMR: δ 206.96, 206.84, 201.85 (t, J_{C-P} = 7.17 Hz) (CO), 144.819(m), 133.39(m), 130.16, 129.23, 128.72, 128.56, 128.15. ^{31}P{^{1}H} δ 7.37 [tm, $^1J_{P-F}$ = 912 Hz, −*P*F$_2$], 39.42 [dm, $^1J_{P-F}$ = 974 Hz, −*P*F(C)]. ^{19}F{^{1}H} NMR: δ −39.84 [d of t, $^1J_{P-F}$ = 973 Hz, $^2J_{P-F}$ = 11.01 Hz, −P*F*(C)], −65.78 [dm, J_{P-F} = 937 Hz, −P*F*$_2$], −69.72 [dm, J_{P-F} = 914 Hz, −P*F*$_2$], −71.00 [dm, J_{P-F} = 926 Hz, −P*F*$_2$]. LRMS: Calcd for $C_{16}H_{12}F_{10}N_6P_6$ $[M - Fe_2CO_6]^+$: 663.9389, Found: 663.4527.

*Compound **3***. Yellow solid, yield: 65 mg, 14.25%. mp: 126−128 °C.Found: C, 28.55; H, 1.46; N, 11.21. Anal. Calcd (%) for $C_{22}H_{10}F_{10}Fe_2N_6O_6P_6$: C, 28.62; H, 1.33; N, 11.13. IR (ν, cm^{-1}): 2962m, 2919m, 2850m, 2069s, 2035s, 1725w, 1613w, 1581w, 1264vs, 1094m, 837s. ^{1}H NMR ($CDCl_3$, ppm): δ 7.55−7.53 (m, 2H, Ph*H*), 7.47−7.38 (m, 3H, Ph*H*), 7.33−7.19 (m, 10H, Ph*H*). ^{13}C {^{1}H} NMR: δ 209.18 (CO), 149.45, 143.13, 139.44, 133.79, 133.74, 130.53, 130.15, 129.02, 128.94, 128.25, 126.26, 116.082, 106.96, 106.76. ^{31}P{^{1}H} δ 7.06 [tm, $^1J_{P-F}$ = 929 Hz, −*P*F$_2$], 26.77 [dm, $^1J_{P-F}$ = 985 Hz, −*P*F(C)], 36.27 [dm, $^1J_{P-F}$ = 973 Hz, −*P*F(C)]. ^{19}F{^{1}H} NMR: δ −44.30 [d of t, $^1J_{P-F}$ = 973 Hz, $^2J_{P-F}$ = 11.30 Hz, −P*F*(C)], −48.19 [d, $^1J_{P-F}$ = 985 Hz, −P*F*(C)], −66.09 [dm, J_{P-F} = 913 Hz, −P*F*$_2$], −70.30 [dm, J_{P-F} = 891 Hz, − P*F*$_2$], −72.88 [dm, J_{P-F} = 892 Hz, −P*F*$_2$]. HRMS: Calcd for $C_{27}H_{16}F_{15}FeN_9O_3P_9$ $[M + H]^+$: 1133.8119, Found: 1133.8069.

*Compound **4***. Red semisolid, yield: 15 mg, 3.00%. IR (ν, cm^{-1}): 2957m, 2918s, 2849m, 2104s, 2063s, 2041s, 1670s, 1463s, 1272vs, 941s, 840s. ^{1}H NMR ($CDCl_3$, ppm): δ 7.41−7.22 (m, 10H, Ph*H*). ^{13}C {^{1}H} NMR: δ 215.49 (Fe−CO), 171.41(C═O), 151.98, 143.05, 139.43, 135.33, 134.81, 130.94, 130.47, 129.16, 128.77, 124.21, 123.65, 116.06, 114.21. ^{31}P{^{1}H} δ 7.92 [tm, $^1J_{P-F}$ = 928 Hz, −*P*F$_2$], 31.58 [dm, $^1J_{P-F}$ = 964 Hz, −*P*F(C)], 41.43 [dm, $^1J_{P-F}$ = 968 Hz, −*P*F(C)]. ^{19}F{^{1}H} NMR: δ −55.44 [d, $^1J_{P-F}$ = 970 Hz, −P*F*(C)], −57.67 [d, $^1J_{P-F}$ = 957 Hz, −P*F*(C)], −68.26 [dm, J_{P-F} = 903 Hz, −P*F*$_2$], −69.45 [dm, J_{P-F} = 917 Hz, −P*F*$_2$]. HRMS: Calcd for $C_{20}H_{10}F_{10}FeN_6O_4P_6$ $[M + Na]^+$: 852.8271, Found: 852.8270.

*Compound **5***. Red solid, yield: 62 mg, 12.37%. mp: 170−172 °C. Found: C, 28.91; H, 1.16; N, 10.11. Anal. Calcd (%) for $C_{22}H_{10}F_{10}Fe_2N_6O_6P_6$: C, 28.94; H, 1.21; N, 10.13. IR (ν, cm^{-1}): 2960m, 2919s, 2851m, 2360m, 2105s, 2064s, 2040s, 1669s, 1267vs, 940s, 876s, 839. ^{1}H NMR ($CDCl_3$, ppm): δ 7.49 (m, 4H, Ph*H*), 7.37 (m, 6H, Ph*H*). ^{13}C {^{1}H} NMR: δ 203.59 (Fe−CO), 171.23(C═O), 130.92, 130.47, 128.77, 127.05 (Ph*C*), 109.33(t, *J* = 13.58). ^{31}P{^{1}H} δ 7.56 [tm, $^1J_{P-F}$ = 903 Hz, −*P*F$_2$], 31.60 [dm, $^1J_{P-F}$ = 973 Hz, −*P*F(C)]. ^{19}F{^{1}H} NMR: δ −55.29 [d, $^1J_{P-F}$ = 974 Hz, −P*F*(C)], −68.14 [dm, J_{P-F} = 906 Hz, −P*F*$_2$], −69.61 [dm, J_{P-F} = 904 Hz, −P*F*$_2$]. HRMS: Calcd for $C_{20}H_{10}F_{10}FeN_6O_4P_6$ $[M + Na]^+$: 852.8271, Found: 852.8271.

Reaction of $P_3N_3F_5$(C≡CPh) with $Fe_2(CO)_9$ in the Presence of Me_3NO. To a solution of anhydrous Me_3NO (68 mg, 0.91 mmol) in dry tetrahydrofuran (THF) (5 mL) was added dropwise a suspension of $Fe_2(CO)_9$ (0.16 g, 0.45 mmol) in THF (10 mL) at −20 °C. The reaction mixture was stirred for 15 min, and a solution of $P_3N_3F_5$(C≡CPh) (0.30 g, 0.91 mmol) in 10 mL of THF was added dropwise. After it was stirred for 15 min at −20 °C, the reaction mixture was slowly brought to room temperature and stirred further for 3 h. Afterward, the reaction mixture was washed with saturated NaCl solution, extracted with ether, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was passed through a short silica gel column to remove decomposed materials. The red fraction obtained was subjected to chromatographic workup using silica gel TLC plates. Use of 1% ethyl acetate/hexane separated compounds **4** (11 mg, 2.92%) and **5** (67 mg, 17.82%).

*Preparation of Compound **6**.* A solution of $Cp(CO)_3Mo-Mo(CO)_3Cp$ (0.19 g, 0.39 mmol) in toluene (30 mL) was refluxed for 12 h under nitrogen. After this solution was cooled, $P_3N_3F_5(C\equiv CPh)$ (0.13 g, 0.39 mmol) in 10 mL of toluene was added, and the reaction mixture was refluxed further for 6 h. The solvent was evaporated by applying vacuum, and the crude mixture was chromatographed through a silica gel column using an ethyl acetate/hexane mixture as the eluent. A red solution came out by eluting at 4% ethyl acetate/hexane, which, on evaporation of the solvent, gave a red semisolid compound characterized as $Cp(CO)_2Mo(P_3N_3F_5)(C\equiv CPh)Mo(CO)_2Cp$ (**6**). Yield: 0.12 g, 40%. mp: 125−127 °C. IR (ν, cm^{-1}): 2956m, 2918m, 2849m, 2360m, 2005s, 1956vs, 1862s, 1258vs, 940s, 816s. ^1H NMR ($CDCl_3$, ppm): δ 5.28 [10H, s, η^5-Cp], 7.44 [d(J = 7.50 Hz), 2H, Ph*H*], 7.32 [d(J = 7.50 Hz), 2H, Ph*H*], 7.13 [t(J = 7.50 Hz), 1H, Ph*H*] . $^{13}C\{^1H\}$ NMR: δ 226.91 and 226.86 (CO), 145.23, 129.10, 128.27, and 126.82 (Ph*C*), 125.29, 101.54, 92.49 (η^5-Cp−Mo). $^{31}P\{^1H\}$ NMR: δ 51.63 [d of t of t, $^1J_{P-F}$ = 973 Hz, $^2J_{P-P}$ = 74.35 Hz, $^3J_{P-F}$ = 16.40 Hz, −*P*F(C)], 8.17 [tm, $^1J_{P-F}$ = 924 Hz, −*P*F$_2$]. $^{19}F\{^1H\}$ NMR: δ −46.56 [d of t, $^1J_{P-F}$ = 973 Hz, $^3J_{P-F}$ = 11.86 Hz, −PF(C)], −67.49 [dm, J_{P-F} = 924 Hz, −P*F*$_2$], −69.02 [dm, J_{P-F} = 926 Hz, −P*F*$_2$]. HRMS: Calcd for $C_{22}H_{15}F_5Mo_2N_3O_4P_3$ $[M]^+$: 768.8304, Found: 769.0881.

*Preparation of Compound **7**.* A solution of $Cp(CO)_3Mo-Mo(CO)_3Cp$ (0.45 g, 0.91 mmol) in toluene (60 mL) was refluxed for 12 h under nitrogen. After this solution cooled, $P_3N_3F_5(C\equiv CFc)$ (0.40 g, 0.91 mmol) in 20 mL of toluene was added, and the reaction mixture was refluxed further for 6 h. The solvent was evaporated by applying vacuum, and the crude mixture was chromatographed through a silica gel column using an ethyl acetate/hexane mixture as the eluent. A red solution emerged by eluting at 2% ethyl acetate/hexane, which, on evaporation of the solvent, gave a deep red crystalline compound characterized as $Cp(CO)_2Mo(P_3N_3F_5)(C\equiv CFc)Mo(CO)_2Cp$ (7). Yield: 0.38 g, 51%. mp: 123−126 °C. Found: C, 37.78; H, 2.30; N, 4.94. Anal. Calcd (%) for $C_{26}H_{19}F_5Mo_2N_3O_4P_3$: C, 38.21; H, 2.34; N, 5.14. IR (ν, cm^{-1}): 2924m, 2854m, 2361m, 2339m, 2017s, 1960vs, 1938vs, 1872s, 1262vs, 1197m, 923s, 822s. ^1H NMR ($CDCl_3$, ppm): δ 5.33 [10H, s, η^5-Cp], 4.40 (s, 2H, −C*H*), 4.31 (s, 2H, −C*H*), 4.17 (s, 5H, Cp*H*). $^{13}C\{^1H\}$ NMR: δ 227.19 and 226.57 (CO), 98.68, 94.19 (d, J = 4 Hz), 92.29 (η^5-Cp-Mo), 85.01, 69.92 (s, Cp), 69.03 (s), and 67.80 (s) [$Cp_{3/4}$ and $Cp_{2/5}$]. $^{31}P\{^1H\}$ NMR: δ 51.36 [d of t of t, $^1J_{P-F}$ = 984 Hz, $^2J_{P-P}$ = 72.65 Hz, $^3J_{P-F}$ = 16.52 Hz, −*P*F(C)], 8.26 [tm, $^1J_{P-F}$ = 910 Hz, −*P*F$_2$]. $^{19}F\{^1H\}$ NMR: δ −46.75 [d of t, $^1J_{P-F}$ = 984 Hz, $^3J_{P-F}$ = 11.44 Hz, −PF(C)], −67.01 [dm, J_{P-F} = 932 Hz, −P*F*$_2$], −68.98 [dm, J_{P-F} = 949 Hz, −P*F*$_2$]. HRMS: Calcd for $C_{26}H_{19}F_5Mo_2N_3O_4P_3$ $[M]^+$: 820.8617, Found: 820.8078.

*Preparation of Compound **8**.* A solution of $Cp(CO)_3Mo-Mo(CO)_3Cp$ (0.20 g, 0.41 mmol) in toluene (60 mL) was refluxed for 12 h under nitrogen. After this solution cooled, $PhC\equiv C-C\equiv CP_3N_3F_5$ (0.15 g, 0.41 mmol) was added, and the reaction mixture was refluxed further for 6 h. The solvent was evaporated by applying vacuum, and the crude product mixture was chromatographed through a silica gel column using a dichloromethane/hexane mixture as the eluent. A dark red solution came out by eluting at 10% dichloromethane/hexane, which, on evaporation of the solvent, gave a dark red crystalline compound characterized as $Cp(CO)_2Mo(P_3N_3F_5)C-C(C\equiv CPh)Mo(CO)_2Cp$ (**8**). Yield: 0.19 g, 0.24 mmol, 59%. mp: 172−174 °C. Found: C, 36.65; H, 1.86; N, 5.41. Anal. Calcd (%) for $C_{24}H_{15}F_5Mo_2N_3O_4P_3$: C, 36.53; H, 1.92; N, 5.32. IR (ν, cm^{-1}): 1935vs, 1864vs (CO), 2195w ($C\equiv C$), 1256s ($P=N$); ^1H NMR: δ 5.44 [10H, s, Cp], 7.30−7.61 [5H, m, Ph]. $^{13}C\{^1H\}$ NMR: δ 77.21, 92.88, 113.61, 123.18, 128.12, 128.24, 131.89. $^{31}P\{^1H\}$ NMR: δ 7.67 [tm, J_{P-F} = 908 Hz, −PF$_2$], 53.22 [dm, $^1J_{P-F}$ = 966 Hz, $^2J_{P-F}$ = 83 Hz, $^3J_{P-P}$ = 15 Hz, −PF(C)], $^{19}F\{^1H\}$ NMR: δ −68.80 [dm, $^1J_{F-P}$ = 928 Hz, −PF$_2$], −68.15[dm, $^1J_{F-P}$ = 886 Hz, −PF$_2$], −52.68 [dm, $^1J_{F-P}$ = 953 Hz, −P*F*(C)]. HRMS: Calcd for $C_{24}H_{15}F_5Mo_2N_3O_4P_3$: 792.8304, Found: 792.8384.

*Preparation of Compound **9**.* A solution of $Cp(CO)_3Mo-Mo(CO)_3Cp$ (0.264 g, 0.54 mmol) in toluene (60 mL) was refluxed for 12 h under nitrogen. After this solution cooled, $FcC\equiv C-C\equiv CP_3N_3F_5$ (0.25 g, 0.54 mmol) was added, and the reaction mixture was refluxed further for 6 h. The solvent was evaporated by applying vacuum, and the crude product mixture was chromatographed through a silica gel column using an ethyl acetate/hexane mixture as the eluent. A dark red solution emerged by eluting at 10% ethyl acetate/hexane, which, on evaporation of the solvent, gave a dark red crystalline compound characterized as $Cp(CO)_2Mo(P_3N_3F_5)C-C(C\equiv CFc)$-$Mo(CO)_2Cp$ (**9**). Yield: 0.25 g, 54%. mp: 169−171 °C. Found: C, 39.78; H, 2.30; N, 4.91. Anal. Calcd (%) for $C_{28}H_{19}F_5Mo_2N_3O_4P_3$: C, 39.98; H, 2.28; N, 4.99. IR (ν, cm^{-1}): 3126w, 2360m, 2181w, 2023s, 1967vs, 1866s, 1252vs, 934s, 914m, 819s. ^1H NMR ($CDCl_3$, ppm): δ 5.42 [10H, s, η^5-Cp], 4.42 (s, 2H, −C*H*), 4.23 (s, 2H, −C*H*), 4.19 (s, 5H, Cp*H*). $^{13}C\{^1H\}$ NMR: δ 226.75 and 225.09 (CO), 93.73, 93.11 (η^5-Cp−Mo), 86.71 (d, J = 5.89 Hz), 82.82 (m), 71.15 (s, Cp), 71.97 (s) and 69.06 (s) [$Cp_{3/4}$ and $Cp_{2/5}$], 65.38. $^{31}P\{^1H\}$ NMR: δ 53.35 [d of t of t, $^1J_{P-F}$ = 951 Hz, $^2J_{P-P}$ = 81.76 Hz, $^3J_{P-F}$ = 15.14 Hz, −*P*F(C)], 7.73 [tm, $^1J_{P-F}$ = 926 Hz, −*P*F$_2$]. $^{19}F\{^1H\}$ NMR: δ −52.53 [dm, $^1J_{P-F}$ = 950 Hz, −PF(C)], −67.61 [dm, J_{P-F} = 934 Hz, −P*F*$_2$], −68.43 [dm, J_{P-F} = 923 Hz, −P*F*$_2$]. HRMS: Calcd for $C_{28}H_{19}F_5Mo_2N_3O_4P_3$ $[M]^+$: 844.8617, Found: 844.8128.

■ CONCLUSION

We have reported the first reactions of alkyne-derived fluorinated cyclophosphazenes with bimetallic metal carbonyls $Fe_2(CO)_9$ and $Cp_2Mo_2(CO)_6$. The reactions of the alkyne with these bimetallic carbonyls behaved differently with the $Fe_2(CO)_9$ reactions, resulting in a range of products based on five-membered ferracyclopentadiene and cyclopentadienone rings bound to $Fe(CO)_3$ moieties, whereas the $Cp_2Mo_2(CO)_6$ reactions resulted in simple tetrahedral complexes similar to those reported for reactions involving $Co_2(CO)_8$. The $Fe_2(CO)_9$ reaction, in addition to the fluorophosphazene-derived ferracyclopentadiene and cyclopentadienone rings bound to $Fe(CO)_3$ moiety also gave an unexpected compound **3**, where a (2,5-diphosphazenyl)cyclopentadienone ring was bound to $Fe(CO)_2(P_3N_3F_5)C=C(Ph)$ unit, where Fe was η^5-bonded to the cyclopentadienone ring, and the alkene carbon that is α to the phenyl unit σ-bonded to the oxygen atom of the cyclopentadienone ring and alkene carbon that is α to the $P_3N_3F_5$ unit is σ-bonded to the Fe atom. $Fe_2(CO)_9$ reaction tried in the presence of trimethylamine N-oxide resulted only in compounds having cyclopentadienone ring bound to the $Fe(CO)_3$ moiety. Also, unlike the reaction of CpCo(COD) with $P_3N_3F_5C\equiv CPh$, no cyclobutadiene derivative bound to $Fe(CO)_3$ or cyclotrimerized products were isolated from this reaction. Unlike $Co_2(CO)_8$, which forms a tetrahedral cluster with geminally disubstituted fluorophosphazene, $P_3N_3F_4(C\equiv CPh)_2$ also $Cp_2Mo_2(CO)_6$ reacts only with the monosubstituted derivatives of $P_3N_3F_5C\equiv CR$ (R = Ph, Fc). The reaction of $N_3P_3F_5(C\equiv C-C\equiv CR)$ with *in situ* generated $Cp_2Mo_2(CO)_4$ indicated the preferential formation of a tetrahedral Mo_2C_2 cluster with the alkyne unit closer to the fluorophosphazene ring selectively. The crystal structure and IR spectral data of these clusters showed the presence of a semibridging carbonyl on one of the molybdenum units. The new iron and molybdenum complexes and cluster compounds showed interesting differences in their spectral and structural properties, and these have been compared.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of selected bond length and bond angles and crystallographic information files (CIF) for compounds **2**, **3**, **5**, **7**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ ACKNOWLEDGMENTS

The authors thank the Department of Science and Technology (DST), India, and the Council of Scientific and Industrial Research (CSIR), India, for financial assistance in the form of research grants to A.J.E (DST (SR/SI/IC-43/2010) and CSIR 01(2693)/12/EMR II). D.K. thanks CSIR India for research fellowship. We thank DST-FIST and IITD for funding of the single-crystal X-ray diffraction and HRMS facilities at IIT Delhi.

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